

STUDIES ON SILVER HALIDE EQUILIBRIA IN MOLTEN POTASSIUM
SODIUM NITRATE

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Sodium Nitrate

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MOLTEN POTASSIUM SODIUM NITRATE.

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This review gives a summary and discussion of results which have been communicated in the following papers. They will be referred to by their Roman numerals.

I. B. Holmberg

Complex Formation between Silver and Iodide Ions in Fused Potassium-Sodium Nitrate. I. A Potentiometric Investigation of the Complex Formation at High Iodide Concentrations.

Acta Chem. Scand. 27 (1973) 875.

II. B. Holmberg

Complex Formation between Silver and Iodide Ions in Fused Potassium-Sodium Nitrate. II. Phase Transformation at High Iodide Concentrations.

Acta Chem. Scand. 27 (1973) 3550.

III. B. Holmberg

Complex Formation between Silver and Iodide Ions in Fused Potassium-Sodium Nitrate. III. Heterogeneous Equilibria Involving Solid and Liquid AgI Solutions.

Acta Chem. Scand. 27 (1973) 3657.

IV. B. Holmberg

Is the Nernst Equation Applicable to Silver(I) Concentration Cells in Fused Nitrate Medium?

Acta Chem. Scand. A 28 (1974) 284.

V. B. Holmberg

Equilibrium Studies in the System $\text{AgBr}-(\text{K},\text{Na})\text{Br}-(\text{K},\text{Na})\text{NO}_3$ at 280 °C and the Significance of Solvation Effects in the Interpretation of Data on Silver Halide Complexation in Nitrate Melts.

Submitted for publication.

VI. B. Holmberg

Cationic Silver Bromide Complexes in Alkali Nitrate Melts.

Submitted for publication.

VII. B. Holmberg

Complex Formation between Silver and Iodide Ions in Fused Potassium-Sodium Nitrate. IV. Cationic Complexes.

Submitted for publication.

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INTRODUCTION

Molten salts form a class of liquids which is rather different from those commonly classified as non-aqueous solvents. Due to their high thermal stabilities and relatively low vapour pressures fused salts can be employed as liquid solvents at temperatures far above the "normal" range. In addition to their unique properties as solvent for such compounds as carbides, nitrides and oxides, their high electrical and thermal conductivity and generally low viscosity have considerably increased the technological importance of molten salts during the past decades. Apart from the well established molten-salt technology involved in the production and purification of metals, there has been a rapidly increasing technological use of inorganic melts in widely different areas such as nuclear reactor technology (as nuclear fuel solvents as well as heat transfer medium), in nuclear fuel reprocessing, in energy storage and conversion systems, as reaction media for e.g. halogenation and halogen exchange reactions of industrial importance,^{1,2} in metal surface treating³ and as catalysts.⁴ Since containment of melts at elevated temperatures is now becoming less and less of a problem, molten salts will most certainly be of increasing technological importance in the future.

As a consequence, needs for better understanding of the fundamental chemical and physical properties of melts have arisen, and research activity in this field has increased very rapidly during the past twenty years. Although the interaction between applied and fundamental fused salt research will most certainly become closer in the future, it should be emphasized that the fundamental study of equilibrium and transport properties of ionic melts is of great importance in itself, since it adds valuable con-

tributions to our understanding of the physics and chemistry of the liquid state. The significant developments in this field have been surveyed recently.⁵⁻¹²

Much recent work has been devoted to the elucidation of the structure of simple ionic liquids. The current opinion is that simple electrostatic requirements preserve some of the crystal structure characteristics in the molten state, i.e. a definite short-range order is present.¹³ On fusion a typical ionic crystalline salt dissociates into its component ions, and, due to coulombic interactions, each ion is preferentially surrounded by oppositely charged ions in a spatial arrangement corresponding to a minimum energy state.

For most salts the density decreases about 20 % upon melting. X-ray and neutron diffraction studies indicate⁶ that the nearest neighbour distances and the coordination numbers are smaller in the melt than in the crystal. These structural features have created a growing interest in the equilibrium solution chemistry of simple fused salts, and have provided the basis for different theoretical approaches to the physical and chemical behaviour of molten salts.^{6,14,15} For simple molten salt mixtures, quasi-lattice models have been applied to rationalize the thermodynamic properties of dilute melts. The models basically consider the ion constituents of the melt as intermixing entities in crystalline-like lattice environments of the solute ions, and accounts for the thermodynamic characteristics of complex ion association in terms of specific bond energies under the assumption of a fixed quasi-lattice coordination number.¹⁶⁻¹⁹ Hence, the non-coulombic interactions are those largely accounted for in such models, and it is obvious that the long range nature of the coulomb interaction forces is difficult to account for in purely theoretical calculations.

In this context it should be noted that the validity of the concept "complex ions" in fused salts - predominantly in binary systems - has been questioned, since it might appear to be difficult to recognize a special group of e.g. anions clustered around a particular cation as being in some way distinct from other similar groups in a binary melt with one kind of anion, where the principle of ionic charge alternation is valid. To-day, however, the "complex ion" concept seems to be well established on the implicit understanding that a complex ion in a purely ionic environment is an entity in which the bonded ligands participate in the random walk of the ion during a time which is longer than that required for a single vibration.

In studies aiming at elucidation of complex formation equilibria in ternary molten salt systems, melts of alkali nitrates and their mixtures have been widely used as solvents, since their properties have been extensively studied.⁹ They have a typical ionic character in the molten state, they have relatively low melting points which facilitate the experimental operations and their thermal stability is good, at least below 300 °C. Furthermore, nitrate ions are expected to form comparably weak complexes with most metal ions, so solvation effects analogous to hydration in aqueous solutions should be expected. The main disadvantage of using nitrates as solvent is that formation and precipitation of heavy metal oxides limits the number of central ions accessible for study, although this disadvantage may be overcome to some extent by the choice of solvent cation composition and temperature.

Since the classical work by Flengas and Rideal,²⁰ who demonstrated the reversible behaviour of silver electrodes in fused nitrate medium, silver(I) has been extensively studied as central ion in complex formation investigations in

nitrate melts, mainly with halide ions as ligands (cf. Refs. 21, 22 and paper VI and references quoted therein). Since the purpose of most of the complex formation studies seems to have been to test the applicability of quasi-lattice models, the data available are widely scattered with respect to solvent composition and temperature, and concern in most cases only such species as AgX , AgX_2^- and Ag_2X^+ with $\text{X} = \text{Cl}$ or Br . Indeed, few attempts at a more complete characterization of stepwise complex formation reactions based on extensive studies with different experimental techniques seem to have been made. It is also evident that collection of experimental data in unsuitable concentration ranges in connection with the use of one single experimental method (predominantly emf measurements) has led to considerable confusion in some cases.^{23,24}

Previous investigations at this laboratory^{22,25} on the formation of silver bromide complexes over a wide range of ligand concentration in equimolar mixtures of KNO_3 and NaNO_3 at 280°C and a preliminary study of the silver iodide complexation in the same medium²⁶ demonstrated that the stepwise formation of mononuclear species AgX , AgX_2^- and AgX_3^{2-} and possibly $\text{Ag}_2\text{X}_6^{4-}$ could be observed, whereas no evidence for a fourth mononuclear complex AgX_4^{3-} was found. This result was in contrast to the behaviour of silver(I) halide systems in aqueous solution, where the existence of AgX_4^{3-} is well established.^{27,28}

The present study was undertaken primarily in order to investigate the influence of the structuring properties of an ionic solvent on the successive building up of complexes between a typical π -acceptor (as classified from aqueous solution studies²⁹) and halide ions with respect to the course of complexation and to the maximum coordination of the central atom. The main interest has been focused to the

silver iodide system, but complementary studies of the bromide complexation have also been performed. The formation of anionic and cationic silver halide complexes in the nitrate melt and the heterogeneous equilibria involved have been investigated in the systems $\text{AgI}-(\text{K},\text{Na})\text{I}-(\text{K},\text{Na})\text{NO}_3$, $\text{AgBr}-(\text{K},\text{Na})\text{Br}-(\text{K},\text{Na})\text{NO}_3$, $\text{AgI}-\text{AgNO}_3-(\text{K},\text{Na})\text{NO}_3$ and $\text{AgBr}-\text{AgNO}_3-(\text{K},\text{Na})\text{NO}_3$.

In order to make this review more perspicuous, the various systems studied and the experimental methods used are schematically presented in Table 1.

EXPERIMENTAL

General

All experimental work was performed at 280°C using equimolar $(\text{K},\text{Na})\text{NO}_3$ as solvent, in order to make meaningful comparisons with previous results^{22,25,26} possible. This solvent composition corresponds to the melting point minimum at 222°C in the binary system $\text{KNO}_3 - \text{NaNO}_3$.

One aim of this study was to find out how different sources of systematic errors of a priori unknown nature can be traced and possibly eliminated by use of various experimental techniques. In particular it was felt desirable to apply different experimental methods to systems $\text{AgI}-(\text{K},\text{Na})\text{I}-(\text{K},\text{Na})\text{NO}_3$, since obvious difficulties in the data interpretation arose in the composition range where the highest complexes were expected to predominate.²⁶

In general, electromotive force measurements in unsaturated solutions and conventional solubility measurements are convenient methods for complex formation studies in fused

Table 1. A brief review of the systems investigated and the different experimental methods used.

(K,Na)NO ₃ systems		Method of study
Additional components	Phases	
AgNO ₃	Homogeneous nitrate melt	Emf
AgNO ₃ + (K,Na)I	Solid solution (K,Na)I + nitrate melt	Solubility of (K,Na)I at various C _{Ag}
AgNO ₃ + (K,Na)I	Solid solution (K,Na)I + nitrate melt	Emf
AgNO ₃ + (K,Na)I	Homogeneous nitrate melt	Emf
AgI + (K,Na)I	Solid solution (Ag,K)I + nitrate melt	Solubility of AgI and distribution of KI between the two phases
AgI + (K,Na)I	Silver iodide melt (Ag,K,Na)I + nitrate melt	Distribution of AgI, KI and NaI between the melts

Composition range	Information gained	Paper
$4 \times 10^{-5} \leq C_{\text{Ag}} \text{ mol}^{-1} \text{ kg} \leq 3$	Thermodynamic ideality	IV
$0 \leq C_{\text{Ag}} \text{ mol}^{-1} \text{ kg} \leq 0.13$	Dependence of $\bar{n}$ on C_{Ag} at fixed $[I^-]$	II
$1 \times 10^{-2} \leq C_{\text{Ag}} \text{ mol}^{-1} \text{ kg} \leq 1 \times 10^{-1}$	Only mono- and dinuclear anionic AgI-species observable	I
$1 \times 10^{-3} \leq C_{\text{Ag}} \text{ mol}^{-1} \text{ kg} \leq 8 \times 10^{-2}$	Stability of AgI_2^- , AgI_3^{2-} I and $\text{Ag}_2\text{I}_6^{4-}$	II, III
$3 \times 10^{-1} \leq C_{\text{I}} \text{ mol}^{-1} \text{ kg} \leq 1.6$	Indication of AgI_4^{3-} (questionable)	
$0.5 \leq C_{\text{I}} \text{ mol}^{-1} \text{ kg} \leq 0.9$	Stability of AgI_3^{2-} and $\text{Ag}_2\text{I}_6^{4-}$	II, III
$8 \times 10^{-3} \leq C_{\text{Ag}} \text{ mol}^{-1} \text{ kg} \leq 3 \times 10^{-2}$		
$0.9 \leq C_{\text{I}} \text{ mol}^{-1} \text{ kg} \leq 2$	Heterogeneous equilibrium constants	II, III
$3 \times 10^{-2} \leq C_{\text{Ag}} \text{ mol}^{-1} \text{ kg} \leq 0.13$		

Table 1 (continued)

AgI+AgNO ₃	Homogeneous nitrate melt	Emf
AgI+AgNO ₃	Silver iodide melt, (Ag,K,Na) (I,NO ₃), + + nitrate melt	Emf
AgI+AgNO ₃	Solid solution Ag(I,NO ₃) + + nitrate melt	Solubility of AgI and distribution of AgNO ₃ between the two phases.
AgI+AgNO ₃	Silver iodide melt, (Ag,K,Na) (I,NO ₃), + + nitrate melt	Distribution of AgI, AgNO ₃ , KNO ₃ and NaNO ₃ between the melts.
AgBr+(K,Na)Br	Solid solution (Ag,Na)Br + + nitrate melt	Solubility of AgBr and distribution of NaBr between the two phases.
AgBr+AgNO ₃	Homogeneous nitrate melt	Emf
AgBr+AgNO ₃	Solid solution Ag(Br,NO ₃) + + nitrate melt	Emf
AgBr+AgNO ₃	Solid solution Ag(Br,NO ₃) + + nitrate melt	Solubility of AgBr and distribution of AgNO ₃ between the two phases.

$1.2 \leq C_{Ag} \text{ mol}^{-1} \text{ kg} \leq 2.4$ $4 \times 10^{-2} \leq C_I \text{ mol}^{-1} \text{ kg} \leq 2 \times 10^{-1}$ $0.7 \leq C_{Ag} \text{ mol}^{-1} \text{ kg} \leq 1.6$ $1.5 \times 10^{-2} \leq C_I \text{ mol}^{-1} \text{ kg} \leq 8 \times 10^{-2}$	The magnitude of the average ligand number $\bar{m}$ and its dependence on C_I	VII
$2.8 \times 10^{-5} \leq C_{Ag} \text{ mol}^{-1} \text{ kg} \leq 7 \times 10^{-1}$ $2.8 \times 10^{-5} \leq C_I \text{ mol}^{-1} \text{ kg} \leq 1.4 \times 10^{-2}$ $7 \times 10^{-1} \leq C_{Ag} \text{ mol}^{-1} \text{ kg} \leq 1.6$ $1.5 \times 10^{-2} \leq C_I \text{ mol}^{-1} \text{ kg} \leq 8 \times 10^{-2}$	Stability of AgI, Ag_2I^+, Ag_3I^{2+} and Ag_4I^{3+} Heterogeneous equilibrium constants	VII
$1 \times 10^{-1} \leq C_{Br} \text{ mol}^{-1} \text{ kg} \leq 2$ $1 \times 10^{-3} \leq C_{Ag} \text{ mol}^{-1} \text{ kg} \leq 1 \times 10^{-1}$	Stability of AgBr_2^-, AgBr_3^{2-} and $\text{Ag}_2\text{Br}_6^{4-}$ Thermodynamics of the solid solution	V
$1.4 \leq C_{Ag} \text{ mol}^{-1} \text{ kg} \leq 2.4$ $3 \times 10^{-2} \leq C_{Br} \text{ mol}^{-1} \text{ kg} \leq 8 \times 10^{-2}$ $0.8 \leq C_{Ag} \text{ mol}^{-1} \text{ kg} \leq 2.2$ $1 \times 10^{-2} \leq C_{Br} \text{ mol}^{-1} \text{ kg} \leq 1 \times 10^{-1}$	The magnitude of the average ligand number $\bar{m}$ and its dependence on C_{Br}	VI
$3 \times 10^{-1} \leq C_{Ag} \text{ mol}^{-1} \text{ kg} \leq 2.2$ $2 \times 10^{-3} \leq C_{Br} \text{ mol}^{-1} \text{ kg} \leq 1 \times 10^{-1}$	Stability of Ag_2Br^+, $\text{Ag}_3\text{Br}^{2+}$ and $\text{Ag}_4\text{Br}^{3+}$ Heterogeneous equilibrium constants	VI

salts. In the present investigation these two methods were supplemented by separate measurements of the ligand solubility (i.e. solubility of $(K,Na)I(s)$) as a function of the $Ag(I)$ concentration and by emf measurements of the "free" central ion concentration in melts saturated in $(K,Na)NO_3$.^{I,II}

During the course of the study it soon became evident that solid solubility phenomena and liquid-liquid immiscibility appeared in cases when melts rather concentrated in ligand were investigated. The heterogeneous equilibria encountered in such systems can be treated neither as conventional solubility equilibria, nor as ordinary solvent extraction equilibria in connection with complex formation studies. New methods of data treatment had to be developed which permit this kind of distribution data to be used for determination of complex compositions and stabilities in the alkali nitrate melt. In addition interesting thermodynamic information on the solid solutions and iodide based melts is gained.^{III,V-VII} This method requires, however, knowledge of the total composition of the halide phase in the entire concentration range under study, a fact that adds some further difficulties to those normally encountered in experimental work at high temperatures.

A considerable amount of data had to be collected in composition ranges where the total concentration of solute species was of an order of magnitude of 1 mol kg^{-1} , in order to analyse the behaviour of the highest complexes. A special study of the thermodynamics of binary solutions $AgNO_3 - (K,Na)NO_3$ was therefore made by emf measurements on silver(I) concentration cells in order to establish the range of ideality exhibited by those simple model solutions.^{IV}

Chemicals and other materials

Commercially available p.a. grade nitrates and alkali metal halides were used without any further purification in all experimental work. Silver halides were prepared by precipitation from aqueous solutions of silver nitrate and potassium halides. The chemicals could be effectively dried by heating at normal atmospheric pressure. The solvent, an equimolar mixture of KNO_3 and NaNO_3 , was prepared by grinding the predried components together to a fine-grained powder for several hours, followed by further drying at 120°C . Equimolar $(\text{K},\text{Na})\text{Br}$ and $(\text{K},\text{Na})\text{I}$ were prepared by a similar process.

It was ascertained in separate experiments that no loss of iodide or bromide due to oxidation by the molten nitrate could be detected.

The experimental work was as a rule performed in normal room atmosphere. In the potentiometric work on anionic silver iodide complexes some experiments were run under dry nitrogen atmosphere for comparison, but no effect on the results could be detected.

The relatively low temperature, 280°C , that was used throughout the whole study, permits ordinary Pyrex glass to be used in vessels and other equipment in contact with the melts. No attack on the glass could be observed after exposure to pure $(\text{K},\text{Na})\text{NO}_3$ melts for periods of about 100 h. When melts concentrated in AgNO_3 were contained in Pyrex vessels for considerable time, a faint yellow colouration of the glass occurred due to silver ion exchange reactions between melt and glass. Nevertheless, such glass equipment could be used repeatedly in work with melts which were very dilute in Ag^+ without any disturbing effects from "back

exchange" phenomena.^{IV}

The electrode material used in the emf studies was spectrographically pure silver wire, spot-welded to a platinum wire, which was sealed into the end of a glass tubing. The electrode surface was silver-plated before use.

It is generally recognized that silver wires become brittle even after a short exposure to a salt melt at high temperature, and migration of silver on the wire has also been observed.³⁰ These disturbing phenomena could be effectively eliminated by minimizing temperature gradients in the electrodes and in a melt layer close to the electrode surface by a careful thermostating procedure.^{IV} Possible corrosion of the silver wires by the nitrate melt will be discussed in a following section.

Electromotive force measurements

The emf measurements were made in a solid aluminium block high-temperature thermostat, which was constructed so as to keep temperature gradients in the test melt at a minimum. The cell container rests in the aluminium block, which is mounted thermally insulated from the surroundings. Reference half-cell vessels, consisting of Pyrex glass tubes with an asbestos fibre sealed through the bottom, are fixed in an aluminium lid, which rests on the top of the main furnace block. The electrodes are mounted in an asbestos lid over the aluminium lid. The furnace is furnished with stoppered observation tubes, which permit occasional visual observation of the test melt under operating conditions. In the first version,^I the furnace heating was effected by a proportional regulator Swema TK 65. Further details of this furnace construction and the temperature mea-

surements are found in paper I.

With this first version of the aluminium block furnace, which was used in the emf study of anionic iodide complexes,^I the maximum time-independent temperature differences in the bulk melt were recorded to be 0.04°C . Considering time-dependent fluctuations as well, the maximum over-all temperature variations amounted to $\pm 0.1^{\circ}\text{C}$ during these emf measurements.

For the study of systems $\text{AgNO}_3 - (\text{K},\text{Na})\text{NO}_3$ and the investigation of cationic complexes the thermostating system was further improved. The temperature was controlled by a fast cycling overshoot-free creep controller, type CR/DHS/PID/SCR from Eurotherm, Worthing, England. In the electrode compartment of the top asbestos lid aluminium blocks were built in. These blocks were separately heated to the temperature of the test melt. Since the upper parts of the electrodes are closely embedded in the heating blocks, transport of heat from the melt through the electrode wires is thought to be effectively eliminated. This improvement in combination with the excellent performance of the Eurotherm regulator decreased the over-all short-time temperature variations in the bulk melt to less than $\pm 0.01^{\circ}\text{C}$ (at 280.08°C on the IPTS-68 scale).

The preliminary check of the validity of Nernst's equation was made by measuring the emf of concentration cells after successive additions of either solidified stock melts of AgNO_3 in $(\text{K},\text{Na})\text{NO}_3$ or pure solid AgNO_3 to halide-free nitrate melts. The emf's were as a rule stable to $\pm 0.3\text{ mV}$ for at least 24 h (paper I). A more systematic study of systems $\text{AgNO}_3 - (\text{K},\text{Na})\text{NO}_3$ was performed in a similar manner with concentrations of AgNO_3 in the reference half-cell

ranging between 0.001 and 1 mol kg^{-1} (paper IV).

Unsaturated melts having iodide in excess over silver(I) were studied by potentiometric central ion concentration measurements. Solid equimolar $(\text{K},\text{Na})\text{I}$ was added to melts with constant C_{Ag} . For each C_{Ag} the maximum range of C_{I} was utilized (see Table 1), which means that most of the concentration range available^{II} has been studied. The composition of the reference half-cell melt was $0.03 \text{ mol kg}^{-1} \text{AgNO}_3$ and $1.3 \text{ mol kg}^{-1} (\text{K},\text{Na})\text{I}$ in order to minimize complications due to AgI precipitation in the asbestos fibre diffusion layer between the half-cells (paper I).

The limited solubility of $(\text{K},\text{Na})\text{I}$ in $(\text{K},\text{Na})\text{NO}_3$ at 280°C was taken advantage of in a study of the formation of polynuclear anionic silver iodide species by a rather "direct" method. AgNO_3 was added in portions to melts saturated in $(\text{K},\text{Na})\text{I}$, and the change in free silver ion concentration with C_{Ag} was registered potentiometrically. One of the experimental advantages of using this method is that effects of junction potentials of unknown magnitude may be minimized by the use of a reference melt which is also saturated in $(\text{K},\text{Na})\text{I}$. Further details are given in paper I.

Cationic silver bromide and iodide complexes were studied by ligand concentration measurements, i.e. $[\text{Ag}^+]$ was measured potentiometrically as C_{Ag} was varied by additions of AgNO_3 to melts having silver(I) in excess over halide. Both unsaturated and saturated nitrate melts were investigated. This study had to be restricted to systems rather concentrated in C_{Ag} and C_{X} in order to minimize the errors in the average ligand number $\bar{m}$ which are due to the small differences $C_{\text{Ag}} - [\text{Ag}^+]$. For $[\text{Ag}^+] > 1 \text{ mol kg}^{-1}$ the relation between $\lg[\text{Ag}^+]$ and the electromotive force E is non-linear

but perfectly reproducible, which is shown in the study of halide-free melts.^{IV} The data from the latter systems were therefore used in support of the determination of ligand numbers $\bar{m}$ from (C_{Ag} ; E) - data pertaining to halide containing systems.

Solubility measurements

Solubilities were measured in melts, contained in Pyrex tubes, thermostated either in an external heating bath of liquid $(K,Na)NO_3$ ^{II,III} or in aluminium block furnaces of principally the same construction as those used for emf measurements.^{V-VII} The systems were agitated by a motor-driven Pyrex propeller. Visual observation of the melts through observation tubes was possible when Al-block furnaces were used. This facility appeared to be very useful in the work with systems where silver halide transitions (s) $\rightarrow$ (l) occurred. After equilibration and phase separation, samples from the nitrate melt were withdrawn with pre-heated thick-walled Pyrex pipettes, quenched and analysed in aqueous solutions.

As a rule no filtration of the saturated melt was required. Occasional filtrations were made by means of a hot glass-filter tube immersed in the melt, but no effects of the filtration could be observed.

The solubility of AgI and the dissolution of KI in the high-temperature form of silver iodide, α -AgI, were studied in a narrow range of C_I .^{II,III} The composition of the solid was determined from the difference between added and found amounts of iodide in the nitrate melt, so relatively large quantities of AgI as compared to $(K,Na)NO_3$ had to be used. Equilibrium times of about 40 h were required.

A separate study of the solubility of (K,Na)I as a function of C_{Ag} was also made in order to analyse the dependence of the ligand number $\bar{n}$ on C_{Ag} at constant $[I^-]$.^{II} In addition, the (K,Na)I solubility was studied at various over-all cation compositions in the system, and a remarkably large cation effect was observed.^{II}

The formation of (Ag,Na)Br solid solutions in systems AgBr - (K,Na)Br - (K,Na)NO₃ was investigated in a series of measurements reported in paper V. The same technique was used as in the iodide systems.

Cationic silver halide complexes were investigated by measurements of the solubility of AgBr or AgI as a function of $[Ag^+]$ in melts having silver(I) in excess over halide, and the composition of the solid solutions Ag(Br,NO₃) and Ag(I,NO₃) was determined as described above.^{VI,VII} The iodide solubility was studied by a radioassay technique by use of ¹³¹I, and the composition of the solid phase was determined separately in systems containing large amounts of inactive AgI. Solid-liquid equilibrium times of about 300 h were required.

Liquid-liquid distribution measurements

In systems AgI - (K,Na)I - (K,Na)NO₃ and AgI - AgNO₃ - (K,Na)NO₃ the silver iodide melts to form a dark red AgI-based liquid, stable in the range $C_I > 0.93 \text{ mol kg}^{-1}$, and a yellow red AgI-based liquid, stable in the range $C_{Ag} > 0.66 \text{ mol kg}^{-1}$, respectively. The distribution of solvent and solute species between the iodide and nitrate melts was studied in experimental arrangements similar to those used for solubility measurements. The phase separation technique is described in paper II.

SYSTEMS $\text{AgNO}_3 - (\text{K}, \text{Na})\text{NO}_3$

The reversible behaviour of $\text{Ag}/\text{Ag(I)}$ electrodes and the approximate validity of the Nernst equation in the form

$$E = E_0 - RTF^{-1} \ln 10 \lg C \quad (1)$$

for concentration cells of the general type



in different fused nitrate media and in various concentration ranges have been verified by several authors.^{20,22,31-46}

This, in turn, has often been taken as a justification for the use of C (expressed as mole fraction or molality) for silver ion activity in the range where eqn. (1) was found to apply. This reflects the general observation that even fairly concentrated solutions in simple ionic melts exhibit remarkably small deviations from ideality. Thermodynamic investigations, extended to the whole composition range of binary systems $\text{AgNO}_3 - \text{MNO}_3$, reveal, however, that the extent of non-ideality, as measured in excess partial molar enthalpies⁴⁷ and free energies,⁴⁴ is strongly dependent on the nature of the cation M^+ . Sodium and potassium ions seem to cause deviations from ideality to approximately the same absolute extent, but the effects are of opposite signs and seem to cancel out largely in equimolar mixtures of KNO_3 and NaNO_3 .⁴⁴

In studies of complex formation equilibria, however, even rather small deviations from ideality, as manifested in an experimental linear relation according to eqn. (1) with a slope deviating by only a small amount, say 1 %, from the theoretical $RTF^{-1} \ln 10$, cannot be ignored. This is so, because such deviations are of a systematic nature and are,

as a rule, outside the limits of uncertainty as predicted from the estimated random errors in the measurements. A systematic deviation of about 1 % from the theoretical value of the Nernst slope might very well mean that the activity factor γ for Ag^+ changes with about 10 % over a composition range of a magnitude generally covered in exhaustive complex formation studies.^{IV}

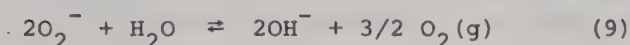
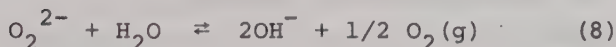
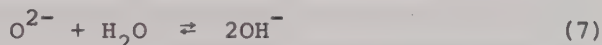
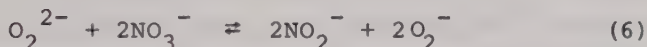
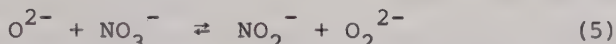
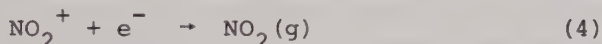
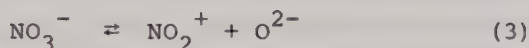
Values of the experimental Nernst slope obtained by several authors in studies on AgNO_3 in equimolar $(\text{K}, \text{Na})\text{NO}_3$ are as a rule smaller than ideal ones by as much as 1 to 5 %.^{20, 22, 34, 46} In order to find out if these observations are indeed indicative of variations in γ or if they are due to systematic errors caused by cooling of the electrode metal surface.^{22, 26} a careful investigation of concentration cells (2) in $(\text{K}, \text{Na})\text{NO}_3$ was undertaken.^{IV}

The results indicate that no systematic deviations from eqn. (1) can be observed in the range $-4 \leq \lg C \text{ mol}^{-1} \text{ kg} \leq 0$, if the temperature is duely controlled. Hence, concentrations on the molality scale can be safely used for Ag(I) activities in this range.

The deviations from linearity in the dilute solution range might be due either to the presence of additional redox systems in minor concentrations, causing a mixed electrode potential, or to the fact that the true C is larger than that calculated from the added amount of AgNO_3 . The latter explanation - which of course by no means rules out the former one - is in agreement with the observations by Conte and Ingram⁴⁸ and by Boxall and Johnson⁴⁴ that corrosion of silver may be of significance in these melts. It is demonstrated in the present study that the deviations are well accounted for by assuming a small constant extra contribu-

tion, d , to the Ag(I) concentration, d being in an order of magnitude of $5 \times 10^{-5} \text{ mol kg}^{-1}$, in all melts after the first reading of a stable emf. Such small values of d do not generally influence the interpretation of data in complex formation studies.

The fact that d differs significantly between different experimental runs (cf. Table 1 in paper IV) suggests that trace impurities, such as H_2O , might influence the extent of corrosion. Such an influence on a redox process in molten alkali nitrates may be understood by considering the following reaction steps:⁴⁹⁻⁵³



An oxidation of Ag via step (4) is of course facilitated by the consumption of oxide ions in step (7) or via a combination of steps (5) and (6) with (8) and (9). Equilibrium constants for reactions (5) - (9) are given in Ref. 53.

In the region $C > 1 \text{ mol kg}^{-1}$ deviations from ideal Nernst behaviour are attributed to the use of molality concentrations instead of mole fractions and to the combined effects of increasing non-ideality and liquid junction potentials. Reasonable estimates of the junction potentials^{44,54} leave a remaining deviation from the straight line of less than 6 mV at $C = 2 \text{ mol kg}^{-1}$. It is of importance to note, how-

ever, that the $(E ; \lg C)$ -relation is perfectly reproducible in this concentrated solution range, a fact that permits emf data to be used in the determination of $[Ag^+]$ in similar systems.^{VI,VII}

THERMODYNAMICS OF SOLID AND LIQUID SILVER HALIDE SOLUTIONS

General

In the high-temperature form of silver iodide, α -AgI, which is stable above 146 °C, the iodide ions are arranged on a body-centered cubic lattice^{55,56} with the silver ions distributed over different cation sites. This special type of crystal structure should obviously facilitate formation of solid solutions with e.g. alkali metal iodides having cation radii close to that of Ag^+ .⁵⁷ Therefore, it could be expected that solid α -AgI in equilibrium with a nitrate melt should form solid solutions to an extent depending on the iodide content of the melt. However, in recently published phase diagrams of systems AgI-MI neither KI nor NaI is reported to dissolve in α -AgI.⁵⁸⁻⁶¹

In the present study^{II} it was found that the transition from a solid AgI phase to an iodide based melt $(Ag,K)I$ was preceded by a rather narrow range where solid solubility of KI in α -AgI occurred to a maximum mole fraction of KI about 0.20 in the solid as the iodide concentration, C_I , in the nitrate melt increases from 0.6 to 0.93 mol kg⁻¹. In the region 0.93 mol kg⁻¹ < C_I < 2.01 mol kg⁻¹ the systems AgI - (K,Na)I - (K,Na)NO₃ consist of two immiscible melts. At $C_I = 2.013$ mol kg⁻¹ a three phase system is reached, which can be described as $(K,Na)I(s) - (Ag,K)I(l) - \text{nitrate melt}$. The observed stability range of $(Ag,K)I$

melts is in perfect agreement with the liquidus range at 280 °C in the binary AgI - KI system according to the phase diagram by Bradley and Greene.⁵⁹

Analogously it was discovered that α -AgI in equilibrium with nitrate melts having silver(I) in excess over iodide dissolves AgNO_3 to a maximum mole fraction of at most 0.19 at 280 °C. At this composition the solid melts to an AgI-based melt $(\text{Ag}, \text{K}, \text{Na})(\text{I}, \text{NO}_3)$, which exists in equilibrium with alkali nitrate melts where $C_{\text{Ag}} > 0.66 \text{ mol kg}^{-1}$.^{VII} It was also discovered that a small but significant solubility of AgNO_3 in AgBr occurs at 280 °C. Solid solutions with the mole fraction of $\text{AgNO}_3 \leq 0.03$ could be prepared by equilibrating AgBr with nitrate melts in the composition range $C_{\text{Ag}} \leq 2 \text{ mol kg}^{-1}$.^{VI}

It is well known that AgBr and NaBr are completely miscible in the solid state at elevated temperatures,⁶²⁻⁶⁵ and it was also found that solid solutions $(\text{Ag}, \text{Na})\text{Br}$ with mole fractions of $\text{NaBr} \leq 0.20$ were formed in systems AgBr - $(\text{K}, \text{Na})\text{Br}$ - $(\text{K}, \text{Na})\text{NO}_3$ in the composition range $C_{\text{Br}} \leq 2.2 \text{ mol kg}^{-1}$ in the nitrate melt.^V

The general impression is that ionic melts are very efficient in equilibrating solids with solutes at elevated temperatures, and it seems that this fact has been largely overlooked both in solution chemistry studies in melts and as a potential tool for preparative work.

Calculation methods

A number of studies on molten salt liquid-liquid distribution equilibria have been reported in the literature,⁶⁶⁻⁷⁰ but obviously all the thermodynamic information lying inherent in the distribution data has never been utilized

to elucidate the complex formation reactions which are coupled with the partition equilibria in such systems.

In order that the solubility and distribution data pertaining to solid or liquid silver halide solution equilibria with nitrate melts might be used quantitatively in the complexation studies, new methods of handling such data had to be developed. The methods, which are described in detail in papers III, V and VII, are based on a formal thermodynamic treatment of the halide phase combined with a complete model description of the nitrate melt in terms of specific ion activities. It is demonstrated in paper V that a less appropriate calculation method used in systems $\text{AgI} - (\text{K}, \text{Na})\text{I} - (\text{K}, \text{Na})\text{NO}_3$ does not violate the results concerning the iodide complexation in any way.

The primary aim of the data treatment has been to evaluate reliable values of the silver halide activity a_1 in the solid or liquid halide phase, in order to calculate the variable ion concentration product $[\text{Ag}^+][\text{X}^-]$ in the alkali nitrate melt. The calculation method, however, permits the evaluation of the activities of all components of the halide phase from the thermodynamic model description - including the complex formation equilibria - of the nitrate melt. Such evaluations have been carried out by different extrapolation techniques, depending on the actual conditioning of experimental data.^{III, V-VII}

Some important features of the calculation method should be noted. Firstly, regarding solid-liquid equilibria, the method is not restricted to cases when a continuous range of solid solution is at hand, but any phase transition may occur as long as the over-all composition of both phases is known. Secondly, random errors in the pertinent composition variables have only a negligible influence on the

result, since the activity a_1 is computed by means of an integration process that largely eliminates such errors. Another advantage of the method is that variations in the $(K,Na)NO_3$ activity, occurring when complex reactions are studied in concentrated melts, are readily detectable. The importance of this will be discussed in conjunction with the anionic complexes in a subsequent section.

Solid silver halide solutions

The equilibrium constants for heterogeneous equilibria determined in papers III and V-VII are collected in Table 2 together with those from previous investigations at this laboratory. (The data on the sodium content in $(Ag,K)I$ melts, given in paper II, have been used without success in attempts to determine NaI activities in these melts.) Components of the solid $AgBr$ and AgI solutions are denoted $(agbrs)$ and $(agis)$, respectively, and those of the AgI -based melts are denoted $(agil)$. The constants originally given in paper III are recalculated to be in agreement with the standard state for the alkali metal ions and nitrate ions used in the subsequent papers V-VII. The use of an activity model for K^+ , referring to fractions $[K^+] / ([K^+] + [Na^+])$ (cf. paper V), instead of concentrations in molality units, brings about a small change in the activities a_2 for KI in the AgI solutions as compared to those given in paper III, whereas the influence on the AgI activity is on the whole negligible. Recalculated activities a_2 are given in the Appendix.

In order to avoid confusion, the equilibrium constants for reactions A, B ... in Table 2 are denoted $K_A, K_B \dots$. The fundamental constant K_D , which is the conventional solubility product for AgI , appears to be well determined. Independent solubility studies^{26,VII} have yielded identical

Table 2. Equilibrium constants for distribution and exchange reactions between silver halide phases and equimolar potassium-sodium nitrate melts at 280 °C. All ionic species are present in the nitrate melt. Standard states and activity scales are specified in the original papers.

Equilibrium reaction	Equilibrium constant	Source
A: $\text{AgBr}(\text{agbrs}) \rightleftharpoons \text{Ag}^+ + \text{Br}^-$	$(3.0 \pm 0.1) \times 10^{-7} \text{ (mol kg}^{-1})^2$	Ref. 22
B: $\text{NaBr}(\text{agbrs}) \rightleftharpoons \text{Na}^+ + \text{Br}^-$	$(9 \pm 1) \text{ mol kg}^{-1}$	V
C: $\text{AgNO}_3(\text{agbrs}) \rightleftharpoons \text{Ag}^+ + \text{NO}_3^-$	$(5.2 \pm 0.6) \times 10^2 \text{ mol kg}^{-1}$	VI
D: $\text{AgI}(\text{agis}) \rightleftharpoons \text{Ag}^+ + \text{I}^-$	$(5.8 \pm 0.1) \times 10^{-10} \text{ (mol kg}^{-1})^2$	Ref. 26, pot.
D: $\text{AgI}(\text{agis}) \rightleftharpoons \text{Ag}^+ + \text{I}^-$	$(6.2 \pm 0.1) \times 10^{-10} \text{ (mol kg}^{-1})^2$	Ref. 26, sol.
D: $\text{AgI}(\text{agis}) \rightleftharpoons \text{Ag}^+ + \text{I}^-$	$(6.2 \pm 0.1) \times 10^{-10} \text{ (mol kg}^{-1})^2$	VII
E: $\text{KI}(\text{agis}) \rightleftharpoons \text{K}^+ + \text{I}^-$	$(5.4 \pm 0.6) \times 10 \text{ mol kg}^{-1}$	III
F: $\text{AgNO}_3(\text{agis}) \rightleftharpoons \text{Ag}^+ + \text{NO}_3^-$	$(3.4 \pm 0.5) \text{ mol kg}^{-1}$	VII
G: $\text{AgI}(\text{agil}) \rightleftharpoons \text{Ag}^+ + \text{I}^-$	$(1.25 \pm 0.08) \times 10^{-9} \text{ (mol kg}^{-1})^2$	III
G: $\text{AgI}(\text{agil}) \rightleftharpoons \text{Ag}^+ + \text{I}^-$	$(1.2 \pm 0.3) \times 10^{-9} \text{ (mol kg}^{-1})^2$	VII
H: $\text{KI}(\text{agil}) \rightleftharpoons \text{K}^+ + \text{I}^-$	$(1.17 \pm 0.04) \text{ mol kg}^{-1}$	III
I: $\text{AgNO}_3(\text{agil}) \rightleftharpoons \text{Ag}^+ + \text{NO}_3^-$	$(1.4 \pm 0.2) \text{ mol kg}^{-1}$	VII
J: $\text{KNO}_3(\text{agil}) \rightleftharpoons \text{K}^+ + \text{NO}_3^-$	$(4 \pm 2) \times 10^2$	VII
K: $\text{NaNO}_3(\text{agil}) \rightleftharpoons \text{Na}^+ + \text{NO}_3^-$	$(1.0 \pm 0.4) \times 10^3$	VII
L: $\text{AgBr}(\text{agbrs}) + \text{Na}^+ \rightleftharpoons \text{NaBr}(\text{agbrs}) + \text{Ag}^+$	$3 \times 10^{-8} \text{ mol kg}^{-1}$	V
M: $\text{AgBr}(\text{agbrs}) + \text{NO}_3^- \rightleftharpoons \text{AgNO}_3(\text{agbrs}) + \text{Br}^-$	$5.8 \times 10^{-10} \text{ mol kg}^{-1}$	VI

N:	$\text{AgI}(\text{agis}) + \text{K}^+$	$\rightleftharpoons \text{KI}(\text{agis}) + \text{Ag}^+$	$1.1 \times 10^{-11} \text{ mol kg}^{-1}$	III
O:	$\text{AgI}(\text{agis}) + \text{NO}_3^-$	$\rightleftharpoons \text{AgNO}_3(\text{agis}) + \text{I}^-$	$1.8 \times 10^{-10} \text{ mol kg}^{-1}$	VII
P:	$\text{AgI}(\text{agil}) + \text{K}^+$	$\rightleftharpoons \text{KI}(\text{agil}) + \text{Ag}^+$	$1.1 \times 10^{-9} \text{ mol kg}^{-1}$	III
Q:	$\text{AgI}(\text{agil}) + \text{NO}_3^-$	$\rightleftharpoons \text{AgNO}_3(\text{agil}) + \text{I}^-$	$8.6 \times 10^{-10} \text{ mol kg}^{-1}$	VII
R:	$\text{AgNO}_3(\text{agil}) + \text{K}^+$	$\rightleftharpoons \text{KNO}_3(\text{agil}) + \text{Ag}^+$	$3 \times 10^{-3} \text{ mol kg}^{-1}$	VII
S:	$\text{AgNO}_3(\text{agil}) + \text{Na}^+$	$\rightleftharpoons \text{NaNO}_3(\text{agil}) + \text{Ag}^+$	$1 \times 10^{-3} \text{ mol kg}^{-1}$	VII
T:	$\text{KNO}_3(\text{agil}) + \text{Na}^+$	$\rightleftharpoons \text{NaNO}_3(\text{agil}) + \text{K}^+$	4×10^{-1}	VII
U:	$\text{KI}(\text{agil}) + \text{NO}_3^-$	$\rightleftharpoons \text{KNO}_3(\text{agil}) + \text{I}^-$	$3 \times 10^{-3} \text{ mol kg}^{-1}$	III, VII

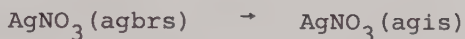
values of K_D , close to that determined potentiometrically by Elding and Leden.²⁶

From studies of the distribution of iodide between solid α -AgI and $(K,Na)NO_3$ melts it is of course impossible to decide whether KI or NaI (or both) is the solute in α -AgI. The low solubility of NaI in liquid AgI at this temperature, further discussed in a following section, strongly suggests, however, that KI is the solute in solid AgI as well. This view has been confirmed by supplementary experiments with systems AgI - NaI - $NaNO_3$ and AgI - KI - KNO_3 at 350 °C.⁷¹

The activity factor for KI in solid $(Ag,K)I$ exhibits a remarkably rapid decrease with increasing KI content in the solution (see Appendix). This pronounced non-ideal behaviour may have its origin in a non-random site occupancy of K^+ in the α -AgI structure, accompanied by a restricted Ag^+ mobility and a perturbation of the iodide lattice.

The solid phase $Ag(I,NO_3)$ exhibits ideal Temkin behaviour,^{VII} which is in sharp contrast to the thermodynamics of the $(Ag,K)I$ solutions. This interesting observation suggests that $Ag(I,NO_3)(s)$ may be regarded as a substitutional solution with iodide and nitrate ions mixing at random on the anion sublattice with negligible enthalpy of mixing. In particular, the partial substitution of iodide for nitrate must not change the accessibility of structurally different cation sites for Ag^+ . Judging from the dimensions of the anions only, the nitrate ion might very well fit into the structure without any considerable perturbation of the anion sublattice.^{55,72} It should be observed, however, that the ideal behaviour ceases close to the melting point composition of the solid, which occurs at a silver nitrate mole fraction of 0.19.

Only a small composition range of $\text{Ag}(\text{Br}, \text{NO}_3)$ solid solutions has been studied, and it is obvious that the partial molar excess free energy for AgBr is close to zero in this range ($x_{\text{AgBr}} \geq 0.97$). The equilibrium constants for the two anion exchange reactions M and O do not differ very much, since the solubility of AgBr - as expressed by reaction A - is considerably larger than that of AgI . The difference between AgBr and AgI in the tendency to form solid solutions with AgNO_3 is evident, however, from the magnitude of the constants K_C and K_F . From these constants the standard free energy change $\Delta G_{CF}^\ominus$ for the transfer of AgNO_3 from AgBr to AgI ,



may be computed as

$$\Delta G_{CF}^\ominus = RT \ln (K_F/K_C)$$

This yields $\Delta G_{CF}^\ominus = -13 \text{ kJ mol}^{-1}$ at 280°C , which reflects not only simple anion size effects, but also the fundamental structural differences between AgBr and AgI at this temperature.

The thermodynamics of solid solutions $(\text{Ag}, \text{Na})\text{Br}$ have been studied previously by miscibility gap calculations,⁶⁵ emf measurements of excess free energies⁶⁴ and calorimetric determination of the enthalpy of mixing.⁷³ Hence, the literature data afford valuable comparison material to test the applicability of the present distribution method. The results from this study^V indicate that activities of AgBr and NaBr in the solid may be rationalized according to a regular solution model⁷⁴ in the range $0.80 \leq x_{\text{AgBr}} < 0.95$, implying non-zero enthalpy of solution formation but ideal mixing entropy, i.e. total randomness in the cation mixing.

The estimated interaction parameter, 9 kJ mol^{-1} , is in good agreement with literature data.^{64,65,73}

Silver iodide melts

Factors that seem to be of importance in determining the extent of liquid-liquid immiscibility in fused salt systems have been thoroughly discussed by several authors.⁷⁵⁻⁷⁸ Differences in ionic radii and polarizabilities between the constituents of the two phases seem to be of significance for phase separation. Generally speaking, differences in the chemical bonding character of the components contribute to the tendency of liquid immiscibility, and it seems appropriate to speak of one "covalent" and one "ionic" melt. In the present study we should thus expect the AgI melt to be the "covalent" one, possessing a high degree of complex association, whereas the predominant structural characteristics of the ionic alkali nitrate melt are those imposed by the requirement of short-range ionic charge alternation.

The thermodynamic similarity between the solid and liquid AgI phase is demonstrated in the magnitude of K_D , $6.2 \times 10^{-10} (\text{mol kg}^{-1})^2$, as compared to K_G , $12 \times 10^{-10} (\text{mol kg}^{-1})^2$. Identical values of K_G were obtained from studies on melts having iodide in excess over silver^{III} and melts having silver in excess over iodide.^{VII} For the hypothetical process



at 280°C the standard free energy change may be computed according to

$$\Delta G_{DG}^\circ = RT \ln (K_G/K_D)$$

This yields $\Delta G_{DG}^{\circ} = (3.2 \pm 0.6) \text{ kJ mol}^{-1}$ which is in excellent agreement with an estimate from a critical compilation of thermodynamic data by Hamer and coworkers,⁷⁹ yielding $\Delta G_{DG}^{\circ} = (3 \pm 1) \text{ kJ mol}^{-1}$.

In extracting alkali metal iodide from a nitrate melt with equal concentrations of K^{+} and Na^{+} , liquid AgI exhibits a remarkable preference for K^{+} . A typical cation composition of the liquid (Ag,K)I phase is 70 % Ag, 30 % K and 0.2 % Na.¹¹ As the soft iodide ions are mixed up with less polarizable nitrate ions, the K^{+} - selectivity decreases markedly as indicated by the constants K_J , K_K and K_T , although K^{+} is still preferred to some extent. The preference for K^{+} is in accordance with the qualitative observations by Kennedy⁷⁰ (systems AgBr - MBr - MNO_3) and Guenther⁶⁹ (systems $HgBr_2$ - MBr - $LiNO_3$), i.e. cations with large polarizing power prefer the "hard" nitrate ion surroundings in the ionic melt. The explanation for this behaviour is probably to be found in the "covalent" melt: the dissolution of e.g. excess halide over silver occurs mainly via silver halide complexation which is most probably favoured by the presence of large alkali metal ions, which compete weakly for halide ions due to their low polarizing power.

The cation size effect, observed in this study, is also in agreement with the magnitude of the partial molar excess free energy $\bar{G}_1^E$ for AgI in binary silver iodide - alkali metal iodide melts, which was determined potentiometrically by Sternberg and coworkers^{80,81} at considerably higher temperatures: for NaI melts $\bar{G}_1^E > 0$ was found whereas $\bar{G}_1^E < 0$ was obtained in KI systems.

In contrast to what is often found for other silver halide based melts⁸, the thermodynamics of the AgI melts studied

in this work cannot be accounted for by assuming regular solution behaviour. It is interesting to note, however, that the deviation from ideality is very much the same in the two kinds of AgI melts.^{III,VII} For example, in systems with $x_{\text{AgI}} = 0.70$ we have $\bar{G}_1^E = -2.4 \text{ kJ mol}^{-1}$ irrespective of whether the main solute is KI or AgNO_3 . It may be tempting to relate this to the fact that the stabilities of anionic and cationic silver iodide complexes are on the whole of the same order of magnitude in the nitrate melt, as will be discussed in a following section. However, little is known about the constitution of the AgI melts. The only structural study of such systems, known to the present author, is a Raman spectroscopy investigation of (Ag,K)I melts.⁸² It was concluded that silver(I) is probably tetrahedrally coordinated.

ANIONIC COMPLEXES

The main interest has been focused on iodide complexes in melts rather concentrated in ligand ($C_I > 0.1 \text{ mol kg}^{-1}$). It is in this region that species with ion charges ≤ -1 predominate, and any investigation aiming at an understanding of the characteristics of the stepwise complex formation in these melts should be performed in this concentration range. On the other hand, in investigations of melts with solute concentrations around 1 mol kg^{-1} difficulties in the data interpretation due to effects which are not considered in the model description used may occur. Three main sources of such effects, *i.e.* systematic errors, will be considered in the following discussion of the results from various kinds of experiments.

The first kinds of errors are those caused by deviations from ideal solution behaviour as the concentrations of

iodide ions and bulky and highly negatively charged complex anions become large. These kinds of errors are thought to be at least partially reduced in the studies of melts, saturated in (K,Na)I, in the sense that variations in activity coefficients, which are due to partial substitution of nitrate ions for iodide ions in the melt, are largely eliminated when $[I^-]$ is kept constant at $1.577 \text{ mol kg}^{-1}$.

From the study of the (K,Na)I solubility as a function of C_{Ag}^{II} , $\bar{n}$ -values were computed from $\bar{n} = (C_I - [I^-])C_{Ag}^{-1}$.

The experimental result may be taken as evidence for polynuclear complexes $Ag_m I_n^{(n-m)-}$ with the ratio $n/m < 3.5$ and possibly a fourth complex AgI_4^{3-} . The accuracy in the $\bar{n}$ -data is, however, rather poor for small C_{Ag} (due to the small differences $C_I - [I^-]$), making the evidence for AgI_4^{3-} of questionable value. In fact, the solubility data are well reproduced within the limits of error by a model, assuming that AgI_3^{2-} and $Ag_2I_6^{4-}$ are the only prevailing complexes.

Apart from the activity factor aspects, there are other advantages associated with potentiometric measurements in melts saturated in (K,Na)I ; there is no need for calculation of the free ligand concentration based on provisional assumptions about the existence of specified complexes and their stability, and the total central ion concentration, C_{Ag} , may be varied over a large range at maximum concentration of free ligand. The experimental results (paper I) provide conclusive evidence that only mono- and dinuclear species are present in observable amounts.

The second kinds of errors are those caused by liquid junction potentials in the concentration cells used in the

potentiometric work. The junction potentials originate in the partial replacement of nitrate ions with iodide ions and complex anions. In the emf measurements in melts having constant $[I^-]$, the junction potential errors due to variations in free iodide ion concentration are eliminated, whereas such errors most probably affect the emf data from unsaturated melts. In the potentiometric study^I the complexes AgI_2^- , AgI_3^{2-} , $Ag_2I_6^{4-}$ and possibly AgI_4^{3-} were identified and their stability determined. It is obvious, however, that the apparent stability of AgI_4^{3-} is influenced by junction potentials of unknown magnitude. A more detailed discussion of these topics is given in paper I.

The third source of systematic errors to be discussed here is rather specific for solution chemistry studies in ionic melts of this kind, although the theoretical implications are of a general nature. In general, complex formation equilibria are schematically represented by use of "naked" ion formulae, such as



with the tacit assumption that effects of solvation of the reactants and products have negligible influence on the equilibrium thermodynamics. This is justified by the fact that the solvent activity is practically constant, since only dilute solutions are studied.

However, the thermodynamic model applied to the nitrate melts made a calculation of the solvent activity possible in two-phase systems. The solubility and distribution data of papers III and V indicate that the nitrate ion activity decreases significantly with increasing halide ion concentration.

This in turn implies that it might be meaningful to make a conceptual distinction between "free" nitrate ions and those attached to silver in the coordination sphere of solvated central ion. Hence, the complex formation equilibria should be strictly looked upon as reversible exchanges of solvent ions, coordinated to the central ion, for ligand ions, producing "free" nitrate ions, i.e. nitrate ions surrounded by alkali metal ions. Although a number of vibrational spectra studies have presented evidence for strong interaction between silver and nitrate ions in pure AgNO_3 (1) and in mixtures of liquid alkali and silver nitrate,⁸³⁻⁹³ there is at present no precise information on the nature of the nitrate-solvated silver ion available. In one of the most interesting Raman spectroscopy studies Clarke and Hartley⁹⁴ attributed the low frequency silver nitrate Raman band at 107 cm^{-1} to a librational oscillation of the nitrate ion about the C_2 axis due to restricted out-of-plane rotation, and concluded that silver ions - as might be expected - are capable of simultaneous association with more than one nitrate ion in mixtures with alkali nitrate.

Solubility and distribution data are especially well suited for testing the "solvation effect" on the determination of stability constants, since the path of integration of the differential expression, involved in the calculation of nitrate activity, is determined by the restriction imposed on the systems by the heterogeneous equilibrium conditions. The experimental data of papers III and V were analysed under three different assumptions about solvated silver ions, $\text{Ag}(\text{NO}_3)_z^{(1-z)}$, namely $z = 0$ (paper III for iodide systems and V for bromide systems), 2 and 4.^V The details of the models with $z > 0$ are found in paper V.

In the pertinent composition range the nitrate ion activity

decreases by at most 20 % as compared to pure $(K,Na)NO_3$ (1). The results concerning the bromide systems clearly show that the conclusions concerning what complex species exist in the melt do not change as z is varied within reasonable limits, and the corresponding apparent stability constants are only moderately influenced.^V

Regarding the iodide system, the solubility and distribution data may be sufficiently well described without considering AgI_4^{3-} , although a somewhat better fit is obtained when AgI_3^{2-} , AgI_4^{3-} and $Ag_2I_6^{4-}$ are all included in the model.^{III,V} The inclusion of nitrate solvation into the model does not help in discriminating between these two alternatives.^V A thorough comparison of the results with those from the potentiometric study is made in paper III.

In testing the solvation model on the potentiometric data it became evident that effects that were ascribed to the presence of AgI_4^{3-} might very well have their origin in the liberation of NO_3^- ions from the solvated silver ions as the iodide complexation proceeds.^V

The results may thus be briefly summarized as follows: In the Ag - Br system the species $AgBr$, $AgBr_2^-$, $AgBr_3^{2-}$ and $Ag_2Br_6^{4-}$ have been observed, whereas no evidence at all can be found for a fourth mononuclear complex.^{22,25,V} In the Ag - I system complexes with the corresponding compositions are detected and weak evidence for AgI_4^{3-} has emerged from the potentiometric study. When possible effects caused by diffusion potentials and solvation phenomena are considered, it appears that the existence of AgI_4^{3-} may be seriously questioned. The stability constants are collected in Table 3.

In Fig. 1 the relative distributions on different species

Table 3. Stability constants β_j for $\text{AgX}_j(j-1)^-$ and $\text{Ag}_j\text{X}(j-1)^+$ and β_{62} for $\text{Ag}_2\text{X}_6^{4-}$ in equimolar $(\text{K}, \text{Na})\text{NO}_3$ at 280 °C.

System	$\text{AgBr}-(\text{K}, \text{Na})\text{Br}$	$\text{AgI}-(\text{K}, \text{Na})\text{I}$	$\text{AgBr}-\text{AgNO}_3$	$\text{AgI}-\text{AgNO}_3$
Source	25, V	26, I, III	25, VI	VII
$\beta_1/\text{mol}^{-1} \text{ kg}$	2.67×10^2	$(4.2 \pm 0.3) \times 10^3$	2.67×10^2	$(4.7 \pm 0.1) \times 10^3$
$\beta_2/\text{mol}^{-2} \text{ kg}^2$	2.3×10^4	$(3.1 \pm 0.3) \times 10^6$	$(1.1 \pm 0.4) \times 10^4$	$(2.43 \pm 0.06) \times 10^6$
$\beta_3/\text{mol}^{-3} \text{ kg}^3$	$(7.0 \pm 0.4) \times 10^4$	$(2.3 \pm 0.3) \times 10^7$	$(2.2 \pm 0.8) \times 10^4$	$(6.3 \pm 1.1) \times 10^6$
$\beta_4/\text{mol}^{-4} \text{ kg}^4$	-	$[(2.8 \pm 0.6) \times 10^6]$	$(4.5 \pm 0.5) \times 10^4$	$(9.7 \pm 0.3) \times 10^7$
$\beta_{62}/\text{mol}^{-7} \text{ kg}^7$	$(3.0 \pm 0.4) \times 10^{10}$	$(1.9 \pm 0.7) \times 10^{16}$	-	-

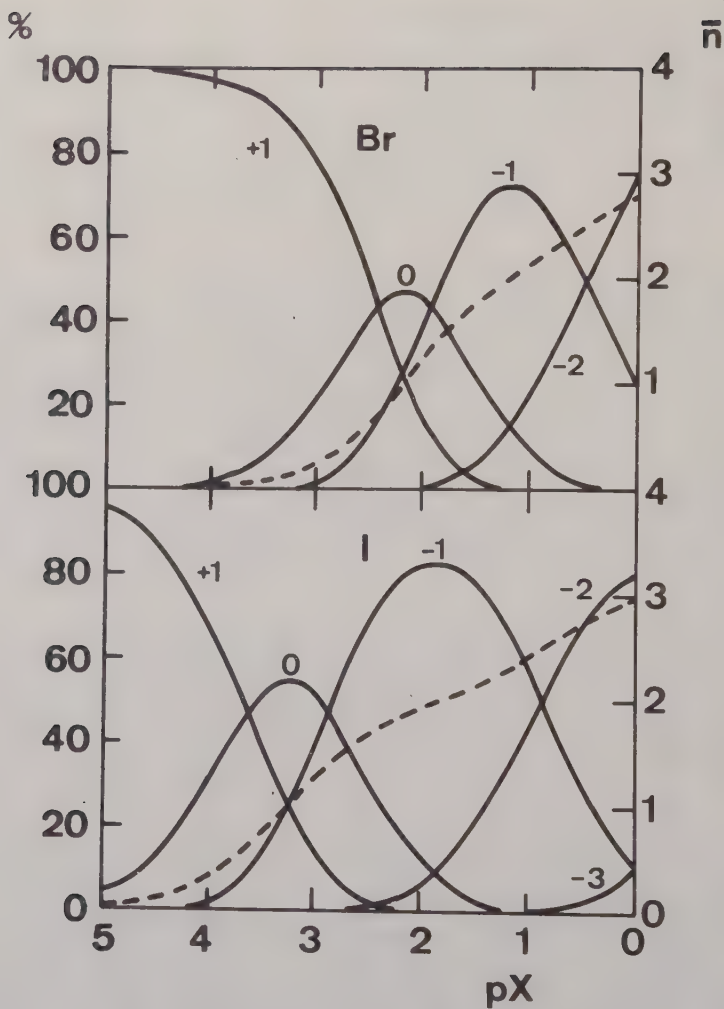


Figure 1. Limiting complex formation curves (dashed) and distributions of Ag on neutral and anionic complexes at $C_{Ag} = 0$, calculated with the constants of Table 3. Ionic charges are marked on the curves.

and the formation curves for the mononuclear anionic complexes are given. Regarding the iodide system, it is evident that AgI_2^- exhibits a pronounced stability relative to AgI and AgI_3^{2-} , as in aqueous solution.⁹⁶ The most striking difference between nitrate melts and aqueous solution is that no clear-cut evidence of AgX_4^{3-} can be found in the melts, whereas the four-coordinated silver halide complexes are well established in aqueous systems.^{27,28,97} One possible explanation of this might be that an introduction of bulky tetrahedral anions into the melts would cause too large a perturbation of the almost close-packed short-range structure of the nitrate melt to be energetically compensated by the creation of a fourth silver halide bond.

CATIONIC COMPLEXES

From studies in aqueous solution the ability of silver and halide ions to form cationic complexes $\text{Ag}_m\text{X}_n^{(m-n)+}$ has become evident, and subsequent investigations in other media, including ionic melts, have also presented convincing evidence for complex cations of this kind. This topic is briefly reviewed in paper VI.

The present study was made by potentiometric ligand concentration measurements, providing experimental ligand numbers $\bar{m}$ in the composition ranges where the difference $C_{\text{Ag}} - [\text{Ag}^+]$ was appreciable, and by solubility/distribution measurements. From the emf measurements it is concluded that no polynuclear (i.e. polybromic and polyiodic) complexes are present in detectable amounts, and hence, the solubility/distribution data are interpreted in terms of species $\text{Ag}_m\text{X}_n^{(m-1)+}$ with $0 \leq m \leq 4$. Table 3 gives the corresponding stability constants. The halide distribution

on different complexes and the formation curves are presented in Fig. 2.

In the bromide system the results concerning β_2 and β_3 are in good agreement with those of Sinistri and Pezzati,⁹⁸ obtained from solubility measurements in equimolar $(K,Na)NO_3$ and apparent β_2 -values in hypothetical pure $KNO_3(l)$ and $NaNO_3(l)$ at 280 °C obtained by extrapolation from the range 400 °C - 500 °C^{35,99} were shown to agree remarkably well with the experimental β_2 from this study.^{VI} The only literature data on cationic iodide complexes in nitrate melts appears to be a value of β_2 , determined potentiometrically in $KNO_3(l)$ at 402 °C by Alvarez-Funes and coworkers.³⁵

The general impression is that the cationic complexation proceeds to approximately the same extent as the anionic one, the iodide complexes being the strongest. From Fig. 2 it is seen that Ag_2I^+ is remarkably stable relative to AgI and Ag_3I^{2+} . A similar, although not so pronounced, stabilization of the second complex is found in the bromide system. This observation is in contrast to what has been found for aqueous solution.¹⁰⁰ No explanation for this difference can be offered at present.

The virtual absence of polynuclear species in nitrate melts is rather interesting in view of the ability of silver(I) to coordinate several halide ions in melts having halide in excess over silver. This observation is, however, in good agreement with results from light absorption¹⁰¹ and self-diffusion¹⁰² measurements in aqueous media; the tendency of condensation in silver halide systems is much smaller - if it occurs at all - on the cationic than on the anionic side.

Regarding the maximum coordination number of halide with

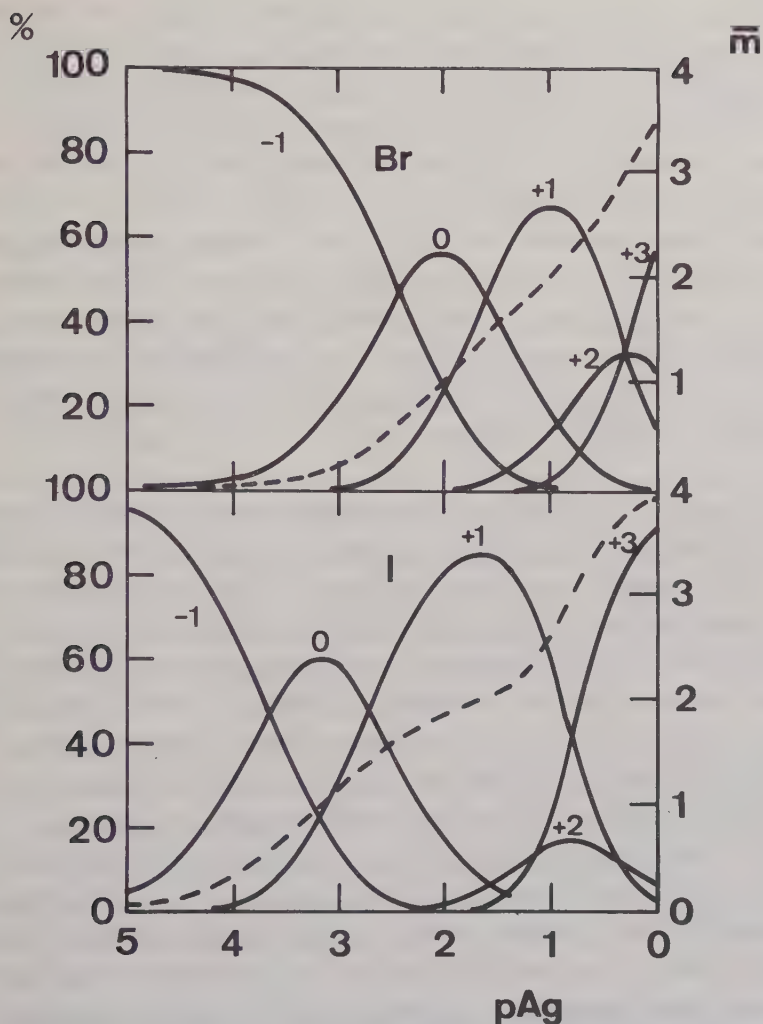


Figure 2. Complex formation curves (dashed) and the distributions of halide on neutral and cationic complexes, calculated with the constants of Table 3. Ionic charges are marked on the curves.

respect to silver(I), there is nothing in the bromide data suggesting higher complexes than $\text{Ag}_4\text{Br}^{3+}$. In the iodide system the emf data seem to indicate a tendency of $\bar{m}$ to take values slightly over 4. However, systematic errors are most probably of an order of magnitude that makes any quantitative interpretation of this small effect in terms of stability constants for Ag_5I^{4+} or higher complexes of little value.^{VII} This circumstance does not by any means exclude the possibility that iodide may coordinate more than four silver ions; the implication is that the maximum coordination number cannot be judged from thermodynamic equilibrium studies of this kind.

In this context structural comparisons with solids of the general formulae $\text{M}_x\text{Ag}_y\text{X}_z$ ($y < z$) and $\text{Ag}_y\text{X}_z\text{A}_x$ ($y > z$) may be made. Such comparisons are especially interesting when the environment of counter-ions (M or A) is the same in the melt and the solid, rendering particle size and short-range packing effects to some extent comparable. From studies of solution equilibria it has become evident that silver coordinates at most four halide ions in anionic complexes. This is well reflected in the structure of compounds $\text{M}_x\text{Ag}_y\text{X}_z$, where the halide ions are arranged in a more or less distorted tetrahedron around silver.¹⁰³⁻¹¹⁴ To the knowledge of the present author the structure of only one compound, which may be regarded as an exception from the rule, has been reported; in $(\text{NH}_4)_6[\text{AuCl}_4]_3\text{Ag}_2\text{Cl}_{15}$ each silver coordinates three chloride ions in an approximately trigonal planar configuration.¹¹⁵

In the case of cationic complexes there is no similar support to be found in crystal structures regarding the halide coordination number. Structures of three compounds $\text{Ag}_y\text{X}_z\text{A}_x$ have been determined. In $\text{Ag}_3\text{I}(\text{NO}_3)_2$ every iodine atom is surrounded by six silver atoms forming a distorted trigonal

prism.¹¹⁶ In Ag_2BrNO_3 the bromine atom is surrounded by five silver atoms in a trigonal bipyramid, and every iodine atom in $\text{Ag}_2\text{IF}\cdot\text{H}_2\text{O}$ has four nearest cation neighbours,¹¹⁷ so no generalization can be made as yet.

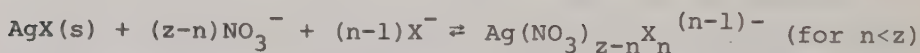
CONCLUDING REMARKS

The structural simplicity and the ideal solvent behaviour of alkali nitrate melts, as demonstrated in paper IV and in the potentiometrically determined solubility products for AgBr^{22} and AgI^{26} in ranges where the solid solution formation is negligible, undoubtedly make such melts attractive for quantitative studies of complexation equilibria. There are, however, mainly two limiting factors which have their origin in pure solvent-solute interactions (i.e. which are not associated with the use of a specific experimental method) to be considered.

As solute concentrations are increased above approximately $1 - 2 \text{ mol kg}^{-1}$, the activity factors for solute species most probably deviate significantly from unity, hereby defining an upper concentration limit which should not be exceeded unless quantitative information on the deviations from ideality is available.

The second limiting factor is the "solvation effect", discussed in detail in paper V. Solvation of halide ions by alkali metal ions in nitrate melts has not been considered,^{VI,VII} since no evidence has been found for such effects in mixed halide nitrate melts.^{86,118,119} Regarding the influence on the interpretation of thermodynamic equilibrium data of liberation of nitrate ions from $\text{Ag}(\text{NO}_3)_z^{(z-1)-}$ as the halide complexation proceeds, it

may be of interest to note, that the interpretation of solubility data with respect to what complexes exist in the melt should not be influenced by the "solvation effect" to the same extent as e.g. emf data. The reason for this is that the dissolution of AgX occurs via processes in which no or only few nitrate ions participate (cf. paper V), e.g.



The real composition of solvated ions such as $\text{Ag(NO}_3\text{)}_z^{(z-1)-}$ and $\text{Ag(NO}_3\text{)}_x\text{X}_n^{(n+x-1)-}$ can of course not be judged from these kinds of thermodynamic measurements, since the solvent activity cannot be varied independent of the solute concentrations. This implies that the relevant structural parameters should be known in order to make a conclusive interpretation of thermodynamic data in terms of stability constants possible in composition ranges where the "solvation effect" may be of significance.

By the discovery of three new kinds of solid solutions, $(\text{Ag,K})\text{I}$, $\text{Ag(I,NO}_3\text{)}$ and $\text{Ag(Br,NO}_3\text{)}$ it has been demonstrated that the high temperature and the potential supply of "naked" ions make ionic melts suitable in feeding solid solvents with solutes. Other experimental evidence from studies of two-phase systems containing silver compounds confirms this observation.¹²⁰ It also appears that a proper thermodynamic analysis of the partition reactions between solid solutions or "covalent" melts and ionic melts can provide useful and interesting information on the thermodynamics of the former solutions. The methods developed here are generally applicable to studies of various kinds of solid-liquid equilibria, including aqueous systems,¹²¹ and liquid-liquid distribution equilibria such as molten

salt extraction processes.

In the silver halide systems studied, the complexation may be characterized as soft acceptor - soft donor^{29,122,123} interactions in a liquid ionic matrix of predominantly hard character. The complex formation in such a system can be readily understood in terms of specific non-coulombic interactions between central ion and ligand. In view of this it would be of great interest to extend the complex formation studies in alkali nitrate melts to harder donors and acceptors which are known to form strong complexes in aqueous solution.

As for the cationic complexes, this study has demonstrated that the silver halide complexation proceeds more readily to highly charged mononuclear complexes on the cationic than on the anionic side. The virtual absence of polymeric cationic species is very interesting, and it is obvious that the nature of the cationic complexes is still rather obscure. A better understanding of the coordination ability of halide ions may be gained from further structural investigations of solids and melts.

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APPENDIX

Recalculated activities a_2 and activity factors f_2 for KI (mole fraction x_2) in solid and liquid AgI solutions. The calculations are performed under the assumptions about the thermodynamic behaviour of alkali nitrate melts made in paper V. Primary data from paper III.

Solid solutions (Ag,K)I

x_2	a_2	f_2
0.02	0.0061	0.3
0.04	0.0065	0.16
0.05	0.0066	0.13
0.11	0.0073	0.07
0.15	0.0076	0.05

Melts (Ag,K)I

x_2	a_2	f_2
0.233	0.36	1.54
0.248	0.39	1.57
0.258	0.42	1.63
0.265	0.44	1.66
0.270	0.45	1.67
0.278	0.48	1.73
0.280	0.48	1.72
0.297	0.54	1.82
0.309	0.57	1.85
0.315	0.60	1.91
0.319	0.61	1.91
0.328	0.64	1.95
0.335	0.66	1.97

